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ON THE AIR-OXIDATION OF AMMONIUM SULPHITE CRYSTALS UNDER ULTRA HIGH PRESSURE.

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Introduction.

The air-oxidation of ammonium sulphite in an aqueous solution has been studied by many investigators under ordinary pressure for over a century. But, on the crystal $(NH_4)_2SO_3$ we have only a few reports, one of which was reported by S. I. Wolfkowitsch and D. L. Tzirlin[1] in 1933. They observed the oxidation of crystal $(NH_4)_2SO_3$ in air at various temperatures under ordinary pressure, and found that, at 20°C, 12.4 % of $(NH_4)_2SO_3$ was converted into $(NH_4)_2SO_4$ in 10 days, at 40°C 59.53 % being converted in 3 days, and at higher temperatures the thermal decomposition occured. From their results it is clear that the oxidation of sulphite is very slow at room temperature under ordinary pressure, and with the rise of temperature the oxidation velocity is increased, but, on account of the thermal decomposition the amount of oxidation has a limit.

We carried out the oxidation of the crystal $(NH_4)_2SO_3$ by compressed air under 500～3,000 kg/cm^2, and measured the amount of conversion of sulphite into sulphate at room temperature.

Experimentals.

(1) The high pressure apparatus and procedure.

The high pressure apparatus used for the present experiments has already been reported[2]. The samples, which ware kept in a brass case, were placed in the pressure chamber (Fig. 1)[3] and compressed by air. The amount of the oxygen consumed in air is, even if $(NH_4)_2SO_3$ is completely oxidized, less than 1 % of the amount of oxygen in the pressure chamber, therfore, it is negligible in the present experiment. And yet, pressure was applied or released so slowly that the temperature changes could be neglected during the operations.

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1) S. I. Wolfkowitsch and D. L. Tzirlin, *Z. anorg. allgem. Chem.*, 211, 257 (1933)
2) R. Kiyama, *This Journal*, 19, 1 (1945)
3) R. Kiyama, and T. Yanagimoto, *This Journal*, 21, 41 (1951).

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(2) The sample.

As $(NH_4)_2SO_3$ was slowly oxidized in air, the sample was prepared for every measurement. The sample was prepared according to the method of Divers and Ogawa[4]. A solution of NH_3 of sp. gr. 0.880 was treated with SO_2, while the flask containing it was kept in a mixture of ice and salt. When the solution turned pasty from the deposition of the crystals of $(NH_4)_2SO_3$, the introduction of SO_2 was stopped. The product, drained on the filter paper, was dried in the vacuum desiccator with KOH for a day.

About 300 mg of the sample was used for each experiment.

(3) The analytical method.

Mostly, $(NH_4)_2SO_3$ was determined by Iodometry. According to Raschig[5], the correct results are always obtained when a sulphite solution is added slowly, with constant stirring, to an iodine solution until the latter is decolorized. Then, a $(NH_4)_2SO_3$ solution is added from a buret to the standard solution of iodine and hydrochloric acid. Simultaneously, the increase in weight due to oxidation, is accurately measured and is found to agree with the result from Iodometry within the experimental allowable error. If necessary, the total nitrogen is also determined by the Kjeldahl method.

Experimental results.

Exp. A: In order to compare with the air-oxidation under high pressure, the amount of the oxidation of crystal $(NH_4)_2SO_3$ under ordinary pressure was measured. The results observed are shown in Table 1.

Table 1

The air-oxidation of $(NH_4)_2SO_3$ under ordinary pressure at 16~20°C

	In air		In desiccator with KOH	
	Purity of $(NH_4)_2SO_3$ (%)	Amount of oxidation (%)	Purity of $(NH_4)_2SO_3$ (%)	Amount of oxidation (%)
Before experiment	84.2		84.2	
After 1 day	82.6	1.90	82.7	1.78
" 2 days	82.2	2.37	82.2	2.37
" 4 days	80.2	4.75	79.5	5.58
" 7*days	74.5	11.52	76.0	9.74

* Only one day was very wet between the 4th and the 7th days.

4) E. Divers and M. Ogawa, *J. Chem. Soc.*, 77, 335 (1900)

5) F. Raschig, *Z. angew. Chem.*, 580 (1904)

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Exp. B: The results of the air-oxidation of crystal $(NH_4)_2SO_3$ under various pressures are shown in Table 2.

Table 2

The air-oxidation of $(NH_4)_2SO_3$ under various pressures.

Pressure applied, kg/cm²	500	2100	3060
Time kept, hrs.	3	3	3
Room temperature, °C	8.0	7.5	10.5
Amount of oxidation from weight (%)	8.06	16.06	98.76
Amount of oxidation from Iodometry (%)	8.10	15.90	98.76

Exp. C: During the measurement of Exp. B, we found a type of $(NH_4)_2SO_3$ which was very stable for oxidation. It is shown in Table 3.

Table 3

The oxidation of difficultly-oxidizable sample of $(NH_4)_2SO_3$.

Presssure applied, kg/cm²	2040	2700
Time kept, hrs.	1	3
Room temperature, °C	9.0	8.5
Amount of oxidation from weight (%)	1.16	7.11
Amount of oxidation from Iodometry (%)	0.99	7.40

As compare with Table 2, the oxidation of sulphite was largely affected according to the sampling.

Exp. D: In order to distinguish the difference between the two samples used in Exp. B and Exp. C, these samples were simultaneously kept in the pressure chamber under the same conditions. The results are shown in Table 4.

Table 4

The oxidation of the two samples under the same conditions.

Pressure: 2,970 kg/cm², Time: 3 hrs., Temp.: 5.1°C.

Samples	$(NH_4)_2SO_3$ used in Exp. B.	$(NH_4)_2SO_3$ used in Exp. C.
Amount of oxidation from weight (%)	97.20	16.48
Amount of oxidation from Iodometry (%)	97.23	16.52

In the above table we can recognize the difference of the stability for air-

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oxidation between the two samples. Therefore, these samples were accurately analysed and the results are shown in Table 5.

Table 5

Results of analysis of two samples of $(NH_4)_2SO_3$.

Samples	Sample used in Exp. B	Sample used in Exp. C
$(NH_4)_2SO_3$	82.33 %	80·88 %
$(NH_4)_2SO_4$	0.42 %	4.75 %
H_2O	17.25 %	14.37 %
Quantity of H_2O in mol	$1\frac{1}{3}$ mol	$1\frac{1}{7}$ mol

As shown in the above table, it is considered that the oxidation velocity is largely affected by the quantity of the water contained.

Exp. E: In order to observe the effect of repeatedly applying and releasing pressure, both sample used in Exp. D were simultaneously kept in the pressure chamber for 30 minutes under 350, 1,000 and 2,000 kg/cm² respectively. Whenever pressure was released, the increase of the weights of both samples were observed, and the total amounts of oxidation were determined by means of Iodometry. The results are shown in Table 6.

Table 6

The oxidation of the two samples in case of applying and releasing pressure.

Temp.: 19°C

		Sample used in Exp. B	Sample used in Exp. C
After 350 kg/cm² (30 min.)	Amount of oxidation (%)	7.82	0.26
After 1,000 kg/cm² (30 min.)	Amount of oxidation (%)	77.09	7.31
After 2,000 kg/cm² (30 min.)	Amount of oxidation (%) from weight	96.55	47.93
	from Iodometry	96.62	47.95

It was apparently recognized that the oxidation of $(NH_4)_2SO_3$ is accelerated by repeatedly applying and releasing pressure.

Exp. F: To compare with cations on the oxidation of sulphites under high pressure, sodium and ammonium salts were simultaneously kept in the pressure chamber and the amount of oxidation measured under the same conditions. The results are shown in Table 7. During this experiment pressure was applied and released over and over again.

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Table 7

The air-oxidation of $(NH_4)_2SO_3$ and Na_2SO_3 under the same conditions.
Pressure applied 300 kg/cm² (immediately released) and 2,040 kg/cm² (3 hrs.).
Temp.: 9.5°C

Samples	Na_2SO_3	$(NH_4)_2SO_3$
Amount of oxidation from weight (%)	0.51	97.58
Amount of oxidation from Iodometry (%)	0.48	97.68

Considerations.

Under ordinary pressure, $(NH_4)_2SO_3$ is slowly oxidized and, as shown in Exp. A, only 10 % of sulphite is converted into sulphate after a week.

Under high pressure, the amount of oxidation rapidly increases under 3,000 kg/cm². The influence of time under pressure is known in Tables 3, 4 and it seems that the time required is considerably long before the reaction reaches an equilibrium. When the pressure was applied and released over and over again, the amount of oxidation was extraordinary increased as shown in Table 6. This behaviour is considered to be caused by the fact that the crystals are shattered and powdered in the course of the procedure and are changed to more easily-oxidizable forms. Therefore, the oxidation is considered to be caused not only by the increase of the collision number on the crystalline surface, but also by the acceleration of the diffusion velocity of oxygen molecules into crystal, and it seems that under 3,000 kg/cm² the diffusion velocity increases rapidly.

From the results in Exp. C, D and E (Table 3, 4 and 6), there are two types of $(NH_4)_2SO_3$ for oxidation. As known in Table 5, the easily and diffcultly-oxidizable samples contains $1\frac{1}{3}H_2O$ and $1\frac{1}{7}H_2O$ respectively. It seems that the amount of oxidation is affected by the quantity of H_2O contained. It is known about ammonium sulphite that there are two types[6], anhydrous $(NH_4)_2SO_3$ and monohydrate $(NH_4)_2SO_3 \cdot H_2O$, and the excessive water in the samples are considered as adherent water among crystals[7]. Therefore, it is considered that the more excessively the sample contains water the more easily it is oxidized.

As shown in Table 7, $(NH_4)_2SO_3$ is much more easily oxidized than Na-salt,

6) Gmelin, *Handb. der anorg. Chem.*, **23**, 256.

7) F. Ishikawa and H. Murooka, *Sci. Papers of the Inst. of Phys. and Chem. Research*, **7**, 1160 (1928)

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and the latter is scarcely oxidized under 2,000 kg/cm^2 for 3 hrs..

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